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(71) Applicant: HALLIBURTON COMPANY
Duncan Oklahoma 73536 (US)

(72) Inventors:
- Eoff, Larry S.
  Oklahoma 73533 (US)
- Kener, Krista L.
  Oklahoma 73533 (US)

(74) Representative: Wain, Christopher Paul et al
A.A. Thornton & Co.
235 High Holborn
London WC1V 7LE (GB)

(54) Well cementing

(57) Subterranean zones penetrated by well bores are cemented using a composition comprised of a hydraulic cement, water in an amount sufficient to form a pumpable slurry and a fluid loss control polymer additive which is made of four monomers, typical of which are the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, the calcium salt of maleic acid, N-vinyl caprolactam and 4-hydroxybutyl vinyl ether.

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Description

[0001] The present invention relates to well cementing methods and compositions.

[0002] Hydraulic cement compositions are commonly utilized in the construction and repair of oil and gas wells. For example, hydraulic cement compositions are used in primary cementing operations whereby strings of pipe such as casing or liners are cemented in well bores. In performing primary cementing, a hydraulic cement composition is pumped into the annular space between the walls of a well bore and the exterior surfaces of a pipe string disposed therein. The cement composition is permitted to set in the annular space thereby forming an annular sheath of hardened substantially impermeable cement therein. The cement sheath physically supports and positions the pipe string in the well bore and bonds the exterior surfaces of the pipe string to the walls of the well bore whereby the undesirable migration of fluids between zones or formations penetrated by the well bore is prevented. Hydraulic cement compositions are also commonly used to plug lost circulation and other undesirable fluid inflow and outflow zones in wells, to plug cracks or holes in pipe strings cemented therein and to accomplish other required remedial well operations.

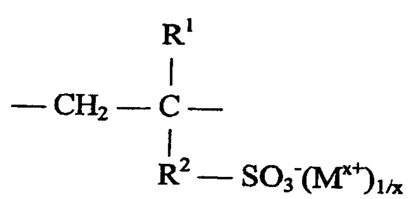
[0003] In order for such well cementing operations to be successful, the cement compositions utilized must include a fluid loss control additive to reduce the loss of fluid, i.e., water, from the cement compositions when they contact permeable subterranean formations or zones. Excessive fluid loss causes a cement composition to be prematurely dehydrated which limits the amount of cement composition that can be pumped, decreases the compressive strength of the cement composition and prevents or reduces bond strength between the set cement composition and a subterranean zone, the walls of pipe and/or the walls of the well bore.

[0004] Heretofore polymers and copolymers have been utilized as fluid loss control additives for well cements. A particularly suitable copolymer which has been utilized as a cement composition fluid loss control additive is a copolymer of 2-acrylamido-2-methyl propane sulfonic acid and N,N-dimethylacrylamide having mole ratios of 2-acrylamido-2-methyl propane sulfonic acid to N,N-dimethylacrylamide of between 1:4 and 4:1 respectively, and having an average molecular weight of between about 75,000 and 3,000,000. While the above described copolymer well cement fluid loss control additive has achieved commercial success, there is a continuing need for improved polymer fluid loss control additives which achieve better fluid loss control in well cement compositions.

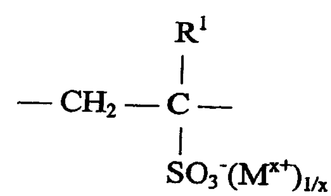
[0005] We have now devised some well cementing compositions which include improved liquid fluid loss control additives comprised of water soluble polymers, which meet the need described above and overcome or mitigate the deficiencies of the prior art.

[0006] In one aspect, the water soluble fluid loss control polymer additives which are useful in accordance with this invention are comprised of the following monomers:

a) 5 to 93 weight % of monomers of the formula (Ia) or (Ib) or both



(Ia)



(Ib)

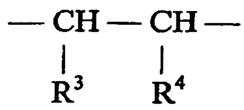
wherein

- R^1 is hydrogen or C_1-C_5 alkyl,
- R^2 is C_1-C_{20} alkylene, carboxy C_1-C_{20} alkylene, carboamido C_1-C_{20} alkylene or phenylene,
- M is hydrogen, ammonium or a metal cation in the oxidation state +I, +II or +III

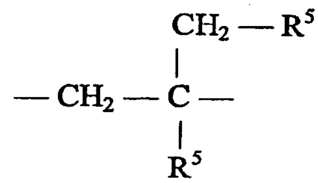
and

- x is 1 to 3;

b) 1 to 50 weight % of monomers of the formula (IIa) or (IIb) or both



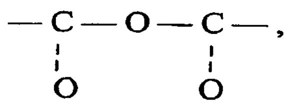
(IIa)



(IIb)

wherein

R^3 and R^4 are $-COO^-(M^{x+})_{1/x}$ or

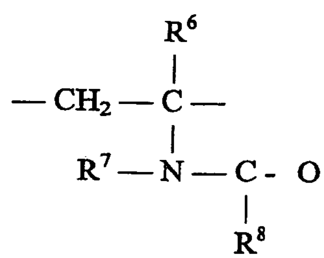


R^5 is $-COO^-(M^{x+})_{1/x}$,
M is hydrogen, ammonium or a metal cation in the oxidation state +I, +II or +III

and

x is 1 to 3;

c) 5 to 93 weight % of a monomer of the formula (III)



(III)

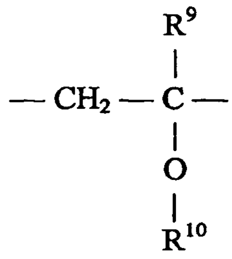
wherein

R^6 is hydrogen or C_1-C_5 alkyl,
R^7 and R^8 are hydrogen, C_1-C_{10} alkyl or $-(CH_2)_y-$

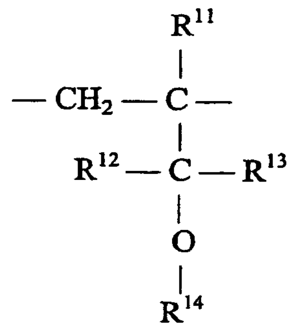
and

y is 3 to 7;

and
d) 1 to 25 weight % of monomers of the formula (IVa) or (IVb) or both



(IVa)



(IVb)

wherein

R^9	is hydrogen or C_1-C_5 alkyl,
R^{10}	is C_1-C_{10} alkyl, C_1-C_{10} aminoalkyl, C_1-C_{20} hydroxyalkyl, C_1-C_4 alkyl or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy (with 1 to 400 alkylenoxy units), C_7-C_{20} alkylaryl, C_7-C_{20} hydroxyalkylaryl, C_6-C_{10} aryl or C_6-C_{10} hydroxyaryl,
R^{11}, R^{12} and R^{13}	are hydrogen or C_1-C_5 alkyl and
R^{14}	is hydrogen, C_1-C_{20} alkyl, C_1-C_{10} aminoalkyl, C_1-C_{20} hydroxyalkyl, C_1-C_4 alkyl- or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy (with 1 to 400 alkylenoxy units), C_7-C_{20} alkylaryl, C_7-C_{20} hydroxyalkylaryl, C_6-C_{10} aryl, C_6-C_{10} hydroxyaryl or with hydroxyl substituted C_1-C_{20} alkylensulfonic acids and their ammonium, alkali metal or alkaline earth metal salts; and

wherein the monomers a) to d) add up to 100 weight %.

[0007] The invention also provides a well cement composition comprising a hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of 2-acrylamido-2-methyl propane sulfonic acid, maleic acid, N-vinyl caprolactam and 4-hydroxybutyl vinyl ether.

[0008] The method of this invention for cementing a subterranean zone penetrated by a well bore comprises placing a cement composition of the invention into the subterranean zone to be cemented and then allowing it to set into an impermeable solid mass therein.

[0009] A preferred fluid loss control polymer additive useful in this invention is a polymer containing the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid in an amount of about 69 weight %, the calcium salt of maleic acid in an amount of about 14 weight %, N-vinyl caprolactam in an amount of about 14 weight % and 4-hydroxybutyl vinyl ether in an amount of about 3 weight %. The polymer additive has a molecular weight of about 250,000.

[0010] The methods of the present invention for cementing a subterranean zone penetrated by a well bore are basically comprised of the following steps. A cement composition is provided comprised of a hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive. The cement composition is placed in the zone to be cemented and thereafter the cement composition is allowed to set into an impermeable solid mass therein. The placement of the cement composition is usually accomplished by pumping the cement composition through the well bore and into the zone to be cemented.

[0011] The cement compositions of this invention are basically comprised of hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive.

[0012] A variety of hydraulic cements can be utilized in accordance with the present invention including, but not limited to, Portland cements, pozzolana cements, gypsum cements, aluminous cements and silica cements. Portland cements are generally preferred with the types defined and described in <u>API Specification For Materials And Testing For Well Cements,</u> API Specification 10, 5th Edition, dated July 1, 1990 of the American Petroleum Institute being particularly suitable. Preferred such API Portland cements include classes A, B, C, G and H with API classes G and H being more preferred.

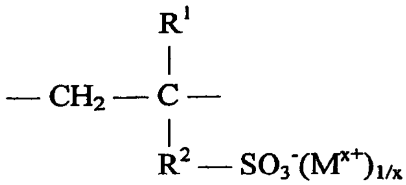
[0013] The water in the cement compositions can be fresh water or salt water. The term "salt water" includes unsaturated salt solutions and saturated salt solutions including brines and seawater. Generally, any water can be utilized so long as it does not adversely affect components of the well cement composition. The water is generally present in a cement composition of this invention in an amount sufficient to form a pumpable slurry, i.e., in an amount in the range

of from about 30% to about 120% by weight of cement in the composition. The water is generally present in the cement composition in an amount in the range of from about 35% to about 100% by weight of hydraulic cement therein.

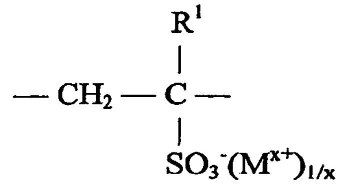
[0014] As mentioned above, the polymeric fluid loss control additives useful in accordance with this invention are water soluble polymers containing four different monomers, the principal monomer being an olefinic sulfonic acid.

[0015] More specifically, the fluid loss control polymers contain:

a) 5 to 93 weight % of monomers of the formula (Ia) or (Ib) or both



(Ia)



(Ib)

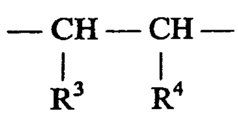
wherein

R^1 is hydrogen or C_1-C_5 alkyl,
R^2 is C_1-C_{20} alkylene, carboxy C_1-C_{20} alkylene, carboamido C_1-C_{20} alkylene or phenylene,
M is hydrogen, ammonium or a metal cation in the oxidation state +I, +II or +III

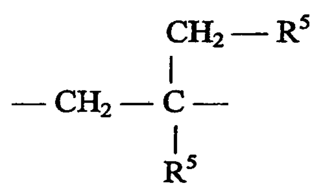
and

x is 1 to 3;

b) 1 to 50 weight % of monomers of the formula (IIa) or (IIb) or both



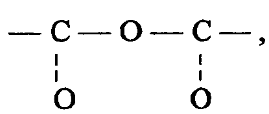
(IIa)



(IIb)

wherein

R^3 and R^4 are $-COO^-(M^{x+})_{1/x}$ or

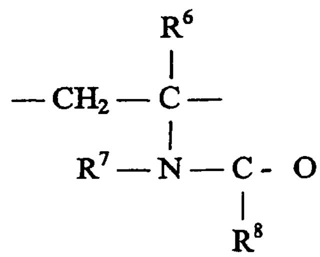


R^5 is $-COO^-(M^{x+})_{1/x}$,
M is hydrogen, ammonium or a metal cation in the oxidation state +I, +II or +III

and

x is 1 to 3;

c) 5 to 93 weight % of a monomer of the formula (III)



(III)

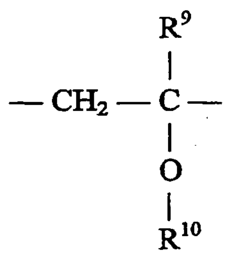
wherein

R^6 is hydrogen or C_1-C_5 alkyl,
R^7 and R^8 are hydrogen, C_1-C_{10} alkyl or -$(CH_2)_y$-

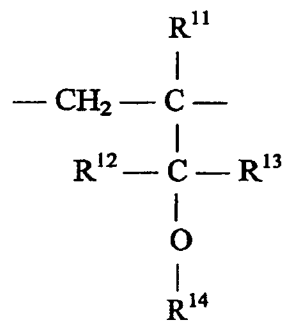
and

y is 3 to 7;

and
d) 1 to 25 weight % of monomers of the formula (IVa) or (IVb) or both



(IVa)



(IVb)

wherein

R^9 is hydrogen or C_1-C_5 alkyl,
R^{10} is C_1-C_{10} alkyl, C_1-C_{10} aminoalkyl, C_1-C_{20} hydroxyalkyl, C_1-C_4 alkyl or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy (with 1 to 400 alkylenoxy units), C_7-C_{20} alkylaryl, C_7-C_{20} hydroxyalkylaryl, C_6-C_{10} aryl or C_6-C_{10} hydroxyaryl,
R^{11}, R^{12} and R^{13} are hydrogen or C_1-C_5 alkyl and
R^{14} is hydrogen, C_1-C_{20} alkyl, C_1-C_{10} aminoalkyl, C_1-C_{20} hydroxyalkyl, C_1-C_4 alkyl- or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy (with 1 to 400 alkylenoxy units), C_7-C_{20} alkylaryl, C_7-C_{20} hydroxyalkylaryl, C_6-C_{10} aryl, C_6-C_{10} hydroxyaryl or with hydroxyl substituted C_1-C_{20} alkylensulfonic acids and their ammonium, alkali metal or alkaline earth metal salts; and

wherein the monomers a) to d) add up to 100 weight %.

[0016] R^1 and R^2 of the monomers of the formulas (Ia) and (Ib) of the fluid loss control polymers of this invention are

preferably hydrogen and -CO-NH-$C(CH_3)_2$-CH-, respectively, and M in the monomers of the formulas (Ia), (Ib), (IIa) and (IIb) are preferably metal cations wherein the +I metal cations are alkali metal ions, most preferably sodium or potassium ions, the +II metal cations are alkaline earth metal ions, most preferably calcium or magnesium ions and the +III metal cations are aluminum or iron ions.

[0017] In the monomer of the formula (III) y is preferably 3 to 5, and in the monomers of the formulas (IVa) and (IVb) when R^{10} and R^{14} are C_1-C_{20} hydroxyalkyl, C_7-C_{20} hydroxyalkylaryl or C_6-C_{10} hydroxyaryl moieties, the moieties can contain one or more hydroxyl functionalities.

[0018] In the monomers of the formulas (IVa) and (IVb), R^9 is preferably hydrogen and R^{10} is preferably one of C_1-C_6 hydroxylalkyl, methyl or hydroxyl terminated mono or poly C_2-C_3 alkenoxy residue. In the monomer of the formula (IVb), R^{11}, R^{12} and R^{13} are preferably hydrogen and R^{14} is preferably 2,3-dihydroxypropyl sulfonic acid, 3-hydroxypropyl sulfonic acid or 2-hydroxypropyl-3-sulfonic acid or the ammonium, alkali metal or alkaline earth metal salts thereof.

[0019] The fluid loss control polymers preferably contain 40 to 83 weight % of the monomers of the formulas (Ia), (Ib) or both, 5 to 48 weight % of the monomers of the formulas (IIa), (IIb) or both, 10 to 53 weight % of the monomer of the formula (III) and 1 to 10 weight % of the monomers of the formulas (IVa), (IVb) or both.

[0020] The fluid loss control polymers preferably have molecular weights in the range of from 10,000 to 3,000,000 grams per mole, more preferably in the range of from 100,000 to 1,000,000 grams per mole.

[0021] A particularly preferred fluid loss control polymer of this invention is comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid (I), 14 weight % of the calcium salt of maleic acid (II), 14 weight % of N-vinyl caprolactam (III) and 3 weight % of 4-hydroxybutyl vinyl ether (IV).

[0022] The fluid loss control polymer additives of this invention can be prepared using known polymerization techniques.

[0023] A fluid loss control polymer additive as described above is included in a cement composition of this invention in an amount in the range of from about 0.1% to about 2% by weight of cement in the composition.

[0024] As will be understood by those skilled in the art, a variety of other well cement composition additives known to those skilled in the art can be included in the cement compositions of this invention. Such additives include, but are not limited to, set retarding additives, set accelerating additives, dispersing agents, lightweight additives and the like.

[0025] A preferred method of cementing a subterranean zone penetrated by a well bore of this invention is comprised of the steps of: (a) providing a cement composition comprising a hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, 14 weight % of the calcium salt of maleic acid, 14 weight % of N-vinyl caprolactam and 3 weight % of 4-hydroxybutyl vinyl ether; (b) placing the composition in the zone to be cemented; and (c) allowing the cement composition to set into an impermeable solid mass therein.

[0026] A more preferred method of cementing a subterranean zone penetrated by a well bore is comprised of the steps of: (a) providing a cement composition comprising Portland cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, 14 weight % of the calcium salt of maleic acid, 14 weight % of N-vinyl caprolactam and 3 weight % of 4-hydroxybutyl vinyl ether present in the cement composition in an amount in the range of from about 0.1% to about 2% by weight of hydraulic cement therein; (b) placing the composition in the zone to be cemented; and

(c) allowing the cement composition to set into an impermeable solid mass therein.

[0027] A preferred well cement composition of this invention comprises a hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, 14 weight % of the calcium salt of maleic acid, 14 weight % of N-vinyl caprolactam and 3 weight % of 4-hydroxybutyl vinyl ether.

[0028] A more preferred well cement composition comprises Portland cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, 14 weight % of the calcium salt of maleic acid, 14 weight % of N-vinyl caprolactam and 3 weight % of 4-hydroxybutyl vinyl ether present in the well cement composition in an amount in the range of from about 0.1% to about 2% by weight of cement in the composition.

[0029] In order to further illustrate the well cementing methods, compositions and additives of the present invention, the following example is given.

EXAMPLE

[0030] A cement composition was prepared containing Portland hydraulic cement, fresh water in an amount of 38% by weight of the cement and a set retarder comprised of a sulfoalkylated lignin. The sulfoalkylated lignin retarder is

described in detail in U.S. Patent No. Re. 31,190 issued to Detroit et al. on March 29, 1983 which is incorporated herein by reference thereto. The cement composition was divided into four test portions. A prior art fluid loss control copolymer additive consisting of a copolymer of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid was added to two of the test cement composition portions in amounts of 1% fluid loss control copolymer additive by weight of cement in the composition. The fluid loss control copolymer additive is described in detail in U.S. Patent No. 4,555,269 issued to Rao et al. on November 26, 1985 which is incorporated herein by reference thereto.

[0031] The fluid loss control polymer additive of this invention was added to the remaining two cement composition test portions in 1% by weight of cement amounts. The particular fluid loss control polymer additive of this invention used was comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, 14 weight % of the calcium salt of maleic acid, 14 weight % of N-vinyl caprolactam and 3 weight % of 4-hydroxybutyl vinyl ether which had a molecular weight of about 250,000. The two cement composition test portions containing the prior art fluid loss control copolymer additives were tested for fluid loss in accordance with the procedure set forth in API Specification 10 mentioned above at temperatures of 100°F and 190°F. In a like manner, the test cement composition portions containing the fluid loss control polymer additive of this invention were tested at 100°F and 190°F. In addition, the portions of the test cement composition were tested for initial viscosity and viscosity after 20 minutes. The results of these tests are given in the Table below.

TABLE

Fluid Loss And Viscosity Tests						
Fluid Loss Control Polymer	Polymer Additive, % by wt. of cement	Set Retarder, % by wt. of cement	Temp ., °F	Fluid Loss, cc/ 30 min.	Initial Viscosity, cp	20 min. Viscosity, cp
A[1]	1	0.2	100	30	25	25
A[1]	1	0.2	190	40	15	25
B[2]	1	0.2	100	18	21	25
B[2]	1	0.2	190	26	18	19

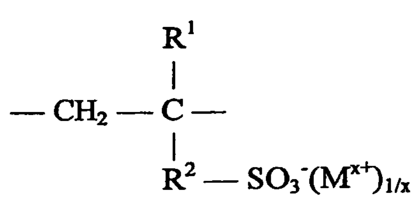
[1]Polymer A was a prior art copolymer comprised of N,N-dimethylacrylamide and 2-acrylamido-2-methyl propane sulfonic acid.
[2]Polymer B was the fluid loss control polymer additive of this invention.

[0032] From the above table, it can be seen that the fluid loss control polymer additive of this invention provides excellent cement composition fluid loss control. Further, the fluid loss control polymer additive of this invention provided better fluid loss control than the prior art fluid loss control copolymer additive.

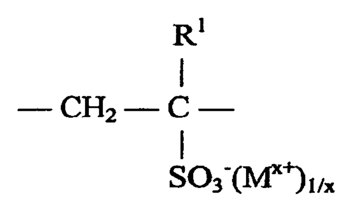
Claims

1. well cement composition comprising a hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of:

   a) 5 to 93 weight % of monomers of the formula (Ia) or (Ib) or both



(Ia)



(Ib)

   wherein

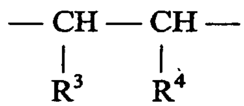
   R^1 is hydrogen or C_1-C_5 alkyl,
   R^2 is C_1-C_{20} alkylene, carboxy C_1-C_{20} alkylene, carboamido C_1-C_{20} alkylene or phenylene,

M is hydrogen, ammonium or a metal cation in the oxidation state +I, +II or +III

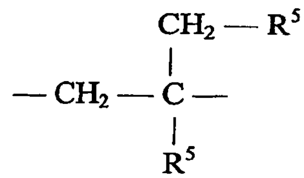
and

x is 1 to 3;

b) 1 to 50 weight % of monomers of the formula (IIa) or (IIb) or both



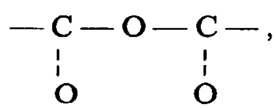
(IIa)



(IIb)

wherein

R^3 and R^4 are $-COO^-(M^{x+})_{1/x}$ or

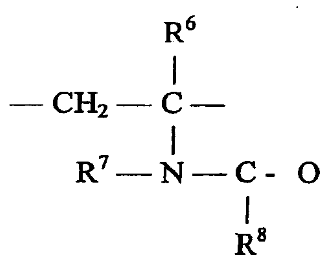


R^5 is $-COO^-(M^{x+})_{1/x}$,
M is hydrogen, ammonium or a metal cation in the oxidation state +I, +II or +III

and

x is 1 to 3;

c) 5 to 93 weight % of a monomer of the formula (III)



(III)

wherein

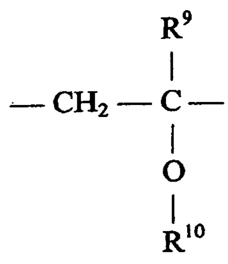
R^6 is hydrogen or C_1-C_5 alkyl,
R^7 and R^8 are hydrogen, C_1-C_{10} alkyl or $-(CH_2)_y-$

and

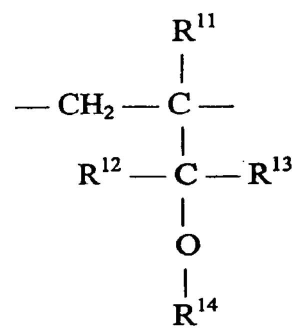
y is 3 to 7;

and

d) 1 to 25 weight % of monomers of the formula (IVa) or (IVb) or both



(IVa)



(IVb)

wherein

R^9	is hydrogen or C_1-C_5 alkyl,
R^{10}	is C_1-C_{10} alkyl, C_1-C_{10} aminoalkyl, C_1-C_{20} hydroxyalkyl, C_1-C_4 alkyl or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy (with 1 to 400 alkylenoxy units), C_7-C_{20} alkylaryl, C_7-C_{20} hydroxyalkylaryl, C_6-C_{10} aryl or C_6-C_{10} hydroxyaryl,
R^{11}, R^{12} and R^{13}	are hydrogen or C_1-C_5 alkyl and
R^{14}	is hydrogen, C_1-C_{20} alkyl, C_1-C_{10} aminoalkyl, C_1-C_{20} hydroxyalkyl, C_1-C_4 alkyl- or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy (with 1 to 400 alkylenoxy units), C_7-C_{20} alkylaryl, C_7-C_{20} hydroxyalkylaryl, C_6-C_{10} aryl, C_6-C_{10} hydroxyaryl or with hydroxyl substituted C_1-C_{20} alkylensulfonic acids and their ammonium, alkali metal or alkaline earth metal salts; and

wherein the monomers a) to d) add up to 100 weight %.

2. A well cement composition comprising a hydraulic cement, sufficient water to form a pumpable slurry and a fluid loss control polymer additive comprised of 2-acrylamido-2-methyl propane sulfonic acid, maleic acid, N-vinyl caprolactam and 4-hydroxybutyl vinyl ether.

3. A composition according to claim 1, wherein R^1 and R^2 of said monomers of the formulae (Ia) and (Ib) are hydrogen and -CO-NH-C(CH_3)$_2$-CH_2-, respectively.

4. A composition according to claim 1 or 3, wherein M in said monomers of the formulae (Ia), (Ib), (IIa) and (IIb) are metal cations wherein said +I metal cations are alkali metal ions, preferably sodium and potassium ions, said +II metal cations are alkaline earth metal ions, preferably calcium and magnesium ions, and said +III metal cations are aluminum or iron ions.

5. A composition according to claim 1,3 or 4, wherein y is from 3 to 5 in said monomer of the formula (III).

6. A composition according to claim 1,3, 4 or 5, wherein when R^{10} and R^{14} in said monomers of the formulae (IVa) and (IVb) are C_1-C_{20} hydroxyalkyl moieties, C_7-C_{20} hydroxyalkylaryl moieties or C_6-C_{10} hydroxylaryl moieties and said moieties can contain one or more hydroxyl functionalities.

7. A composition according to claim 1,3,4,5 or 6, wherein in said monomers of the formulae (IVa) and (IVb), R^9 is hydrogen and R^{10} is a C_1-C_6 hydroxylalkyl or a methyl or hydroxyl terminated mono- or poly-C_2-C_3 alkylenoxy residue.

8. A composition according to claim 1,3,4,5,6 or 7, wherein in said monomer of the formula (IVb), R^{11}, R^{12} and R^{13} are hydrogen and R^{14} is 2,3-dihydroxypropyl sulfonic acid, 3-hydroxypropyl sulfonic acid or 2-hydroxypropyl-3-sulfonic acid or their ammonium, alkali metal or earth alkaline metal salts.

9. A composition according to claim 1, or any of claims 3 to 8, wherein said fluid loss control polymer additive contains 40 to 83 weight % of said monomers of the formula (Ia) or (Ib) or both, 5 to 48 weight % of said monomers of the formulas (IIa) or (IIb) or both, 10 to 53 weight % of said monomer of the formula (III) and 1 to 10 weight % of said monomers of the formulas (IVa) or (IVb) or both.

10. A composition according to any of claims 1 to 9, wherein said fluid loss control polymer additive has a molecular weight in the range of from 10,000 to 3,000,000 grams per mole, preferably from 100,000 to 1,000,000 grams per mole.

11. A composition according to any of claims 1 to 10, wherein said fluid loss control polymer additive is present in said cement composition in an amount of from 0.1% to 2% by weight of cement in the composition.

12. A composition according to any of claims 1 to 11, wherein said hydraulic cement is a Portland cement, pozzolana cement, gypsum cement, aluminous cement or silica cement.

13. A composition according to any of claims 1 to 12, wherein said water is fresh water or salt water, and is preferably present in an amount from 35% to 100% by weight of cement of said composition.

14. A composition according to any of claims 1 to 13, wherein the fluid loss control polymer additive is comprised of 69 weight % of the calcium salt of 2-acrylamido-2-methyl propane sulfonic acid, 14 weight % of the calcium salt of maleic acid, 14 weight % of N-vinyl caprolactam and 3 weight % of 4-hydroxybutyl vinyl ether.

15. A method of cementing a subterranean zone penetrated by a well bore comprising the steps of:

(a) placing a cement composition as claimed in any of claims 1 to 14, in said subterranean zone to be cemented; and
(b) allowing said cement composition to set into an impermeable solid mass therein.

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 03 25 3302

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 4 674 574 A (SAVOLY ARPAD ET AL) 23 June 1987 (1987-06-23) * column 5, line 31 - line 56 * ---	1-15	E21B33/13 C04B24/24
A	US 5 039 433 A (SOPKO THOMAS M ET AL) 13 August 1991 (1991-08-13) * column 2, line 55 - column 4, line 12 * * claims 41-53 * -----	1-15	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

E21B
C04B

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
MUNICH	7 October 2003	Zimpfer, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 03 25 3302

Claim(s) searched completely:
2, 10-15

Claim(s) searched incompletely:
1, 3-9

Reason for the limitation of the search:

Present claims 1 and 3-9 relate to an extremely large number of possible compounds. Support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC is to be found, however, for only a very small proportion of the compounds claimed

In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the polymer comprising, as claimed in claim 2, AMPS, maleic acid, N-vinyl caprolactam and 4-hydroxybutyl vinyl ether as monomers.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 25 3302

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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07-10-2003

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82